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ARYL TELLURIUM TRIHALIDES—I

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Abstract—New aryl tellurium trichlorides have been prepared. A method for synthesizing aryl tellurium tribromides and triiodides based on the halogenolysis of the corresponding ditellurides is presented. Thiophenoxtellurine was obtained from *o*-thiophenoxyphenyltellurium trichloride.

Aryl tellurium trichlorides (III) were prepared by Morgan *et al.*[1] [3] by the action of tellurium tetrachloride on aromatic compounds having an activated *para* position.

$$\underset{\text{I}}{\text{Ar—H}} + \underset{\text{II}}{\text{TeX}_4} \longrightarrow \text{HX} + \underset{\text{III}}{\text{ArTeX}_3}$$
$$\text{X} = \text{Cl}$$

This method was used later by Reichel and Kirschbaum[4] for preparing compounds of type III and by Reichel and Ilberg[5] who synthesized tellurium trichlorides derived from quinoline. Campbell and Turner[6] developed a method based on the reaction of organic mercury compounds with tellurium tetrachloride in dioxane.

$$\underset{\text{IV}}{\text{Ar—Hg—X}} + \underset{\text{II}}{\text{TeX}_4} \xrightarrow{\text{diox}} \underset{\text{III}}{\text{ArTeX}_3} + \text{HgX}_2 \cdot \text{dioxane}$$
$$\text{X} = \text{Cl}$$

The advantage of this procedure used by Farrar[7] and by Rheinboldt and Vicentini[8], permits the use of aromatic compounds without activated *para* positions.

In this work several aryl tellurium trichlorides including three new ones (III: Ar = *p*-C_6H_5—S—C_6H_4, 1-$C_{10}H_7$, XI; Table 1) were prepared.

These compounds were reduced with sodium sulphide in accordance with Reichel and Kirschbaum[9] giving rise to the corresponding diaryl ditellurides (V) (Table 1).

$$\underset{\text{III}}{2\,\text{ArTeCl}_3} \xrightarrow{\text{Na}_2\text{S.9H}_2\text{O}} \underset{\text{V}}{\text{Ar—Te—Te—Ar}}$$

The preparation of di-*p*-hydroxyphenylditelluride (V: Ar = *p*-HO—C_6H_4) was not possible due to decomposition with separation of tellurium. The use of mild reducing agents led to the same results.

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* Present address: Escola Politécnica da U.S.P. Praça Cel. Fernando Prestes, 74 São Paulo, Brasil. The experimental part of this work was executed in 1953, being part of the thesis oriented by the late Prof. H. Rheinboldt.

[1] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.* 2307 (1925).

[2] G. T. Morgan and R. E. Kellett, *J. Chem. Soc.* 1080 (1926).

[3] M. D. K. Drew, *J. Chem. Soc.* 233 (1926).

[4] L. Reichel and E. Kirschbaum, *Liebigs Ann.* **523**, 211 (1936).

[5] L. Reichel and K. Ilberg, *Ber. Dtsch. Chem. Ges.* **76**, 1108 (1943).

[6] I. G. M. Campbell and E. Turner, *J. Chem. Soc.* 39 (1938).

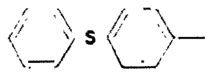
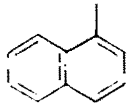
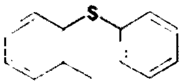
[7] W. V. Farrar, *Research* **4**, 177 (1951); *Chem. Abstr.* **45**, 7543 (1951).

[8] H. Rheinboldt and G. Vicentini, *Chem. Ber.* **89**, 624 (1956).

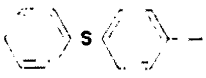
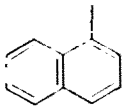
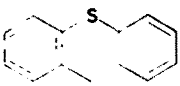
[9] L. Reichel and E. Kirschbaum, *Ber. Dtsch. Chem. Ges.* **76**, 1105 (1943).

Very little is known of the aryl tellurium tribromides. Morgan *et al.*[2,3] described incompletely two tribromides while Vicentini *et al.*[10] prepared 2-naphtyltellurium tribromide (III: Ar = $2\text{-}C_{10}H_7$; X = Br).

TABLE 1. ARYL TELLURIUM TRICHLORIDES: $ArTeCl_3$

Compound: Ar –	M.p.	Appearance	Analyses Te % Calc.	Analyses Te % Found
	164·5–165·5 (dec)	dark yellow needles from glacial acetic acid	30·44	30·60
	175–180° (dec)	yellow crystals from glacial acetic acid	35·33	35·14
	213–215°	yellow needles from glacial acetic acid	30·44	30·40

DIARYL DITELLURIDES: ArTeTeAr

Compound: Ar –	M.p.	Appearance	Analyses Te % Calc.	Analyses Te % Found
	89–90°	red needles from petroleum ether (50–70°)	40·78	40·41
	123·5–124·5	red needles from petroleum ether (50–70°)	50·08	49·82
	130·5–131	orange red needles from petroleum ether (50–70°)	40·78	40·71

Aryl tellurium triiodides were unknown until the present. The synthesis of these compounds using tellurium tetrabromide and tellurium tetraiodide is not recommended due to the low reactivity of these tellurium tetrahalides.* The preparation of tribromides and triiodides by halogenolysis of the ditellurides (V) proceeds without difficulty and in quantitative yield (Tables 2 and 3).

$$V + 3X_2 \longrightarrow \underset{\text{III}}{2ArTeX_3}$$

$$X = Br, I$$

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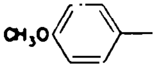
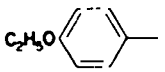
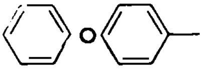
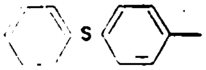
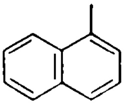
* H. Rheinboldt. Private communication.

[10] G. Vicentini, E. Giesbrecht and L. R. M. Pitombo, *Chem. Ber.* 92, 40 (1959).

TABLE 2. ARYL TELLURIUM TRIBROMIDES
$Ar—TeBr_3$

Compound: Ar —	M.p.	Appearance	Analyses Te%	
			Calc.	Found
	188–190° (dec)	yellow needles from acetic acid	26·89	26·81
	195–205° (dec)	yellow plates from acetic acid	26·12	26·53
	206·5–207°	yellow orange plates from acetic acid	23·78	23·61
	206–207°	yellow orange plates from acetic acid or benzene petroleum ether (50–70°)	23·09	23·11
	159–160° (dec)	red orange needles from benzene-petroleum ether (50–70°)	25·80	25·85

In this connexion it is interesting to point out that the halogenolysis of the diaryl diselenides gives rise to aryl selenium trihalides[11] and to aryl selenenyl halides[12] depending on the molar proportion of the halogen used:

$$\underset{\text{VI}}{ArSeSeAr} + 3X_2 \longrightarrow \underset{\text{VII}}{2ArSeX_3} \qquad X = Cl, Br$$

$$\underset{\text{VI}}{ArSeSeAr} + X_2 \longrightarrow \underset{\text{VIII}}{2ArSeX}$$

Aryl selenium trihalides are not stable, and can give rise to aryl selenenyl halides by loss of halogen:[13]

$$ArSeX_3 \longrightarrow ArSeX + X_2$$

The attempt to prepare the tellurenyl halides by the controlled halogenolysis of diaryl ditellurides (1 mole of ditelluride : 1 mole of halogen) was not successful, indefinite compounds being obtained,* with the exception of 2-naphtyltellurenyl iodide, prepared in pure and crystalline form.[10]

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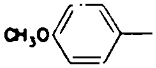
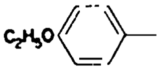
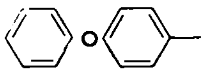
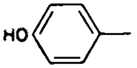
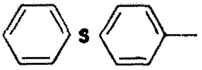
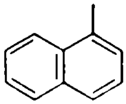
* H. Rheinboldt. Private communication.

[11] Houben-Weyl, *Methoden der Organ. Chemie* (IVth Ed.) pp. 1130, 1132. Georg Thieme Verlag, Stuttgart (1955).

[12] Houben-Weyl, *Methoden der Organ. Chemie* (IVth Ed.) pp. 1161, 1164. Georg Thieme Verlag, Stuttgart (1955).

[13] Houben-Weyl, *Methoden der Organ. Chemie* (IVth Ed.) pp. 1162, 1166. Georg Thieme Verlag, Stuttgart (1955).

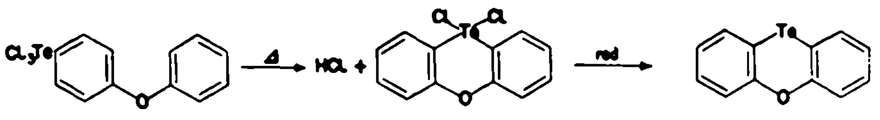
TABLE 3. ARYL TELLURIUM TRIIODIDES
$ArTeI_3$

Compound: Ar =	M.p.	Appearance	Analyses Te%	
			Calc.	Found
	131–133° (dec)	small black crystals from benzene	20·73	21·04
	133–134° (dec)	black needles from benzene	20·27	20·27
	160·5–161° (dec)	red-black plates from benzene–petroleum ether (50–70°)	18·83	18·84
	125–150° (dec)	small dark-red brilliant crystals from water sulphuric acid	21·21	21·18
	180° (dec)	small dark red crystals from benzene–petroleum ether (50–70°)	18·39	18·52
	133° (dec)	black brilliant needles from benzene–petroleum ether (50–70°)	20·07	20·07

The preparation of *p*-hydroxyphenyltellurium tribromide and triiodide by this method is impossible due to the nonexistence of the corresponding ditelluride. Meanwhile the triiodide (III: Ar = *p*-HO—C_6H_4; X = I) was prepared by the reaction of the corresponding trichloride with a solution of potassium iodide.

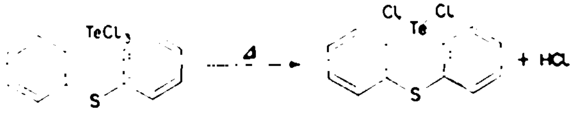
This reaction fails when potassium bromide is used, the starting material being recovered unchanged.

Drew[3] found that by heating *p*-phenoxyphenyltellurium trichloride (III: Ar = *p*-C_6H_5—O—C_6H_4) at a temperature above its melting point a cyclization involving rearrangement occurs, and 10,10-dichlorophenoxtellurine (IX) is formed. This compound was reduced to the phenoxtellurine (X).



III IX X

When *p*-thiophenoxyphenyl tellurium trichloride (III: Ar = *p*-C_6H_5—S—C_6H_4) was similarly treated with the purpose of obtaining 10,10-dichlorothiophenoxtellurine (XII), decomposition occurred. This cyclic sulphur tellurium compound was prepared starting from the *ortho* derivative (XI).

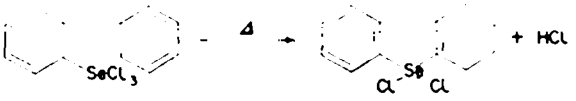


XI XII

By reduction of XII with sodium sulphide thiophenoxtellurine (XIII) was obtained in very good yield.

XIII

A similar reaction is shown by *o*-biphenylylselenium trichloride (XIV)



XIV

EXPERIMENTAL

Trichlorides

p-*Thiophenoxyphenyltellurium trichloride* (III: Ar *p*-C_6H_5—S--C_6H_4). A solution of 9·3 g (0·05 mole) diphenyl sulphide and 13·5 g (0·05 mole) tellurium tetrachloride in 20 cc chloroform was refluxed for 40 hr, an evolution of hydrogen chloride being noted. The dark crystalline product was dissolved in benzene and precipitated with petroleum ether (50–70°). Crude trichloride (8·8 g, 42% yield) was purified from glacial acetic acid or from a mixture of benzene and petroleum ether (50–70°) as dark yellow needles m.p. 164·5–165·5° (dec).

p-Methoxyphenyltellurium trichloride (III: Ar *p*-CH_3—O·-C_6H_4; m.p. 191–193°), *p*-ethoxyphenyltellurium trichloride (III: Ar *p*-C_2H_5–O—C_6H_4; m.p. 179–180°), *p*-phenoxyphenyltellurium trichloride (III: Ar *p*-C_6H_5—O—C_6H_4; m.p. 156–157°), and *p*-hydroxyphenyltellurium trichloride (III: Ar · *p*-HOC_6H_4; m.p. 223–227° (dec) were prepared in accordance with the procedure of Reichel and Kirschbaum[4] and Drew[3].

1-*Naphtyltellurium trichloride* (III: Ar 1-$C_{10}H_7$). A solution of 7·2 g (0·02 mole) 1-naphtyl mercury chloride[14] and 5·4 g (0·02 mole) tellurium tetrachloride in 40 cc pure dioxane was refluxed for 2 hr. The dioxane mercury chloride complex that precipitates on cooling was removed by filtration. The dark yellow solution was concentrated to a viscous oil. On cooling and adding petroleum ether (50–70°) the oil solidified and was separated by filtration and dried on a porous plate. The crude trichloride (8·8 g) was contaminated with dioxane mercury chloride complex giving a 96% yield calculated on the ditelluride. Recrystallization from glacial acetic acid furnished yellow crystals m.p. 175–180° (dec).

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[14] A. N. Nesmejanow, *Ber. Dtsch. Chem. Ges.* **62**, 1010 (1929).

o-*Thiophenoxyphenyl mercury chloride*. Sodium nitrite (12 g, 0·166 mole) was added to a mixture of 40 g (0·166 mole) *o*-thiophenoxyaniline hydrochloride, (prepared reducing 2-nitrodiphenyl sulphide with Fe/acetic acid; m.p. 36°) 75 cc conc hydrochloric acid and 80 g ice, keeping the temperature at 0–5°. To the filtrate was added, dropwise, with stirring, a solution of 45·1 g (0·166 mole) of mercury chloride in 100 cc cold hydrochloric acid (50%). During the addition the temperature must be maintained at 0°. An orange yellow precipitate formed and stirring was continued for 30 min. The product was filtered, washed with water, with alcohol and finally with ether, yielding the diazonium salt mercury chloride complex (75 g, 88·7%). A suspension of the complex in 270 cc acetone was cooled to −60°, treated with 18·2 g metallic copper (freshly prepared), and the temp. maintained at −60° for 12 hr and then slowly brought to normal temp. The brown product was filtered, extracted with acetone and the yellow solution allowed to crystallize, yielding 54·5% (33 g). Recrystallization from alcohol furnished colourless plates m.p. 135–136°. (Found S, 7·63. $C_{12}H_9ClHgS$ requires: S, 7·61%).

o-*Thiophenoxyphenyltellurium trichloride* (XI). Starting with 8·4 g (0·02 mole) of *o*-thiophenoxyphenyl mercury chloride and proceeding as in the case of 1-naphtyltellurium trichloride, 9·6 g crude trichloride contaminated with dioxane mercury chloride complex was obtained. The yield calculated on the basis of the ditelluride is 80·6%. Recrystallization from glacial acetic acid gave yellow needles m.p. 213–215°.

Aryl tellurium trichlorides solubilities. They are very soluble in cold methanol and ethanol, soluble in both glacial acetic acid and chloroform, sparingly soluble in benzene, insoluble in carbon tetrachloride and petroleum ether.

Ditellurides (Table 1)

Di-p-*thiophenoxyphenylditelluride* (V: Ar = *p*-$C_6H_5SC_6H_4$). *p*-Thiophenoxyphenyltellurium trichloride (0·42 g, 0·001 mole) was added to 3·6 g (0·015 mole) hydrated sodium sulphide (Na_2S—$9H_2O$) and heated at 95–100°. The reaction was exotermic and the di-*p*-thiophenoxyphenylditelluride separated as a red oil, the temp being maintained unchanged for 15 min. The mixture was then diluted with water, and on cooling the ditelluride separated out quantitatively.

In the same manner di-1-naphtylditelluride, di-*o*-thiophenoxyphenylditelluride (Table 1) and the known di-*p*-methoxyphenylditelluride[2,4] (m.p. 59–60°), di-*p*-ethoxyphenylditelluride[1,4] (m.p. 107°), di-*p*-phenoxyphenylditelluride[3] (m.p. 88–88·5) were prepared.

In the case of *p*-hydroxyphenyltellurium trichloride a decomposition occurred, forming tellurium. Sodium bisulphite, zinc in chloroform, hydrazine sulphate and phosphorous acid were all tried without success.

The diaryl ditellurides are soluble in cold benzene, chloroform and carbon tetrachloride, and in warm methanol, ethanol, glacial acetic acid and petroleum ether (50–70°).

Tribromides (Table 2)

p-*Methoxyphenyltellurium tribromide* (III: Ar = *p*-$CH_3OC_6H_4$). To a cold solution of 0·47 g (0·001 mole) di-*p*-methoxyphenylditelluride was added dropwise with stirring 0·48 g (0·003 mole) bromine dissolved in a few cc carbon tetrachloride. The *p*-methoxyphenyltellurium tribromide separated quantitatively as an orange solid.

In the same manner *p*-ethoxyphenyltellurium tribromide, *p*-phenoxyphenyltellurium tribromide, *p*-thiophenoxyphenyltellurium tribromide, 1-naphtyltellurium tribromide were prepared.

The *p*-hydroxyphenyltellurium trichloride treated with potassium bromide in benzene was recovered unchanged.

The tribromides show solubilities similar to the corresponding trichlorides.

Triiodides (Table 3)

p-*Methoxyphenyltellurium triiodide* (III: Ar = *p*-$CH_3OC_6H_4$). The procedure was similar to that used for the corresponding tribromides. The yields were quantitative with exception of *p*-methoxyphenyltellurium triiodide obtained in a 93% yield. The *p*-hydroxyphenyltellurium triiodide was prepared by treating a solution of the corresponding trichloride in methanol with excess aqueous potassium iodide.

The triiodides are sparingly soluble in the usual organic solvents but are soluble in dioxane. An exception is *p*-hydroxyphenyltellurium triiodide which is soluble in water, methanol and ethanol.

10,10-*Dichlorothiophenoxtellurine* (XII). *o*-Thiophenoxyphenyltellurium trichloride (2·1 g, 0·005 mole) was heated at 240–250° in a glass tube with stirring for 30 min. Evolution of HCl was noted. On cooling, the dark liquid solidified to a dark yellow mass (1·9 g). This was dissolved in acetone, the solution filtered from a small residue of tellurium and crystallized, yielding needles (0·8 g, 42%), m.p. 265–270° (at 230°, a change in the crystalline form was noted). (Found Te, 33·24. $C_{12}H_8Cl_2STe$ requires: Te, 33·34%).

Thiophenoxtellurine (XIII). To 0·8 g (0·002 mole) of XII 7·2 g (0·03 mole) hydrated sodium sulphide was added and heated at 100° for 15 min. The reaction mixture was diluted with water and the product filtered and dried (0·6 g, 96%). Recrystallization from ethanol gave pale yellow needles m.p. 122–123·5°. (Found Te, 40·90. $C_{12}H_8STe$ requires: Te, 40·92%).